Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

Bis(1-*tert*-butyl-1*H*-imidazole-κN^3)-dichloridocobalt(II)

Eberhardt Herdtweck,[a]* Alexander Zeller[a] and Thomas Strassner[b]

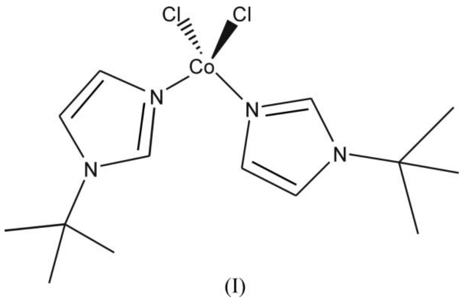
[a]Department Chemie, Lehrstuhl für Anorganische Chemie, Technische Universität München, Lichtenbergstrasse 4, D-85747 Garching bei München, Germany, and [b]Lehrstuhl für Physikalische Organische Chemie, Technische Universität Dresden, Bergstrasse 66, D-01069 Dresden, Germany
Correspondence e-mail: eberhardt.herdtweck@ch.tum.de

Received 3 April 2012
Accepted 8 May 2012
Online 30 May 2012

In the crystal structure of the title compound, [CoCl$_2$(C$_7$H$_{12}$N$_2$)$_2$], molecular units are formed by coordination of the unsubstituted N atoms of two *tert*-butyl-substituted imidazole molecules and two chloride ligands, which distinguishes the complex from structures of imidazolium-based dications with tetrachloridocobaltate dianions. There are two crystallographically independent molecules in the asymmetric unit, related by a noncrystallographic inversion centre.

Comment

We have previously reported the syntheses of hexakis(1-isopropylimidazole)calcium(II) dichloride, [Ca(^{i}PrIm)$_6$]Cl$_2$, and di-μ-chlorido-bis[tris(1-*tert*-butylimidazole)chloridocalcium(II)], [(^{t}BuIm)$_3$CaCl(μ_2-Cl)$_2$ClCa(^{t}BuIm)$_3$], as well as the complex triaquatris(1-isopropylimidazole)magnesium(II) dichloride, [Mg(^{i}PrIm)$_6$(H$_2$O)$_3$]Cl$_2$ (Unger *et al.*, 2007). In these cases, we synthesized the complexes from the respective imidazoles and alkaline earth metal salts. We report here the synthesis of bis(1-*tert*-butyl-1*H*-imidazole-κN^3)dichloridocobalt(II), (I), starting from the bis-imidazolium salt.



(I)

In the asymmetric unit of (I) there are two crystallographically independent molecules, *A* (including atom Co1) and *B* (atom Co2) (Fig. 1). They are related by a noncrystallographic inversion centre. As can be seen from the Cl—Co—N—C torsion angles (Table 1), the core geometry of molecules *A* and *B* differs only slightly. The Co$^{\rm II}$ cation of (I) is coordinated in a distorted tetrahedral geometry by two chloride ligands (Table 1) and two 1-*tert*-butyl-1*H*-imidazole ligands, which coordinate *via* N atoms. These bond lengths are not significantly longer than in the analogous methyl-substituted complex bis(methylimidazole)CoCl$_2$ (Mukerjee *et al.*, 2000). Even the N—Co—N angle is comparable [^{t}Bu = 109.65 (7)° for molecule *A* and 116.50 (8)° for molecule *B* *versus* Me = 110.6 (1)°], which shows that the steric demand of the larger *tert*-butyl group has no influence on the coordination geometry. The most obvious difference is that in the methyl-substituted case, the imidazole ligands have approximate *anti* orientations, while in (I), the ligands are approximately *syn*, with the ethylene groups of the rings on the same side of the complex. By quenching the reaction with elemental sulfur we could show that the free carbene is formed under the

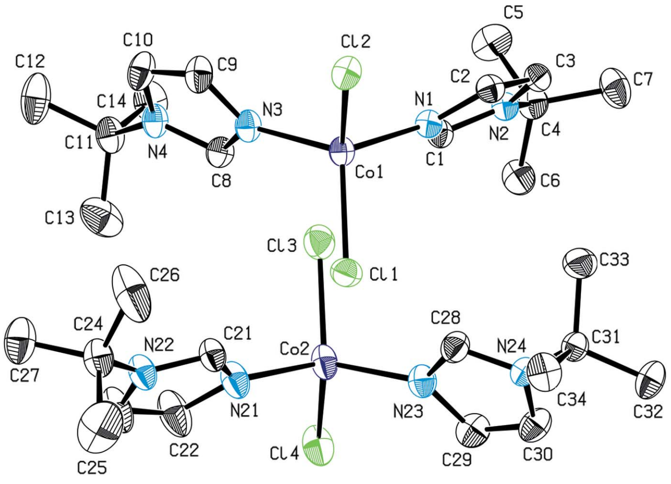


Figure 1
A perspective view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

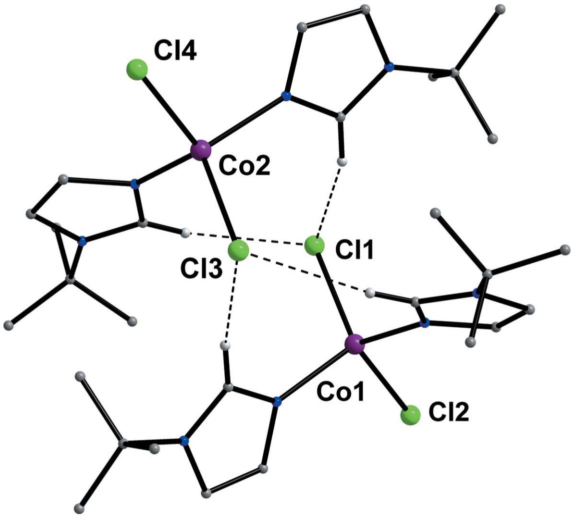


Figure 2
The head-to-tail arrangement of molecules *A* and *B*. Dashed lines indicate hydrogen bonds.

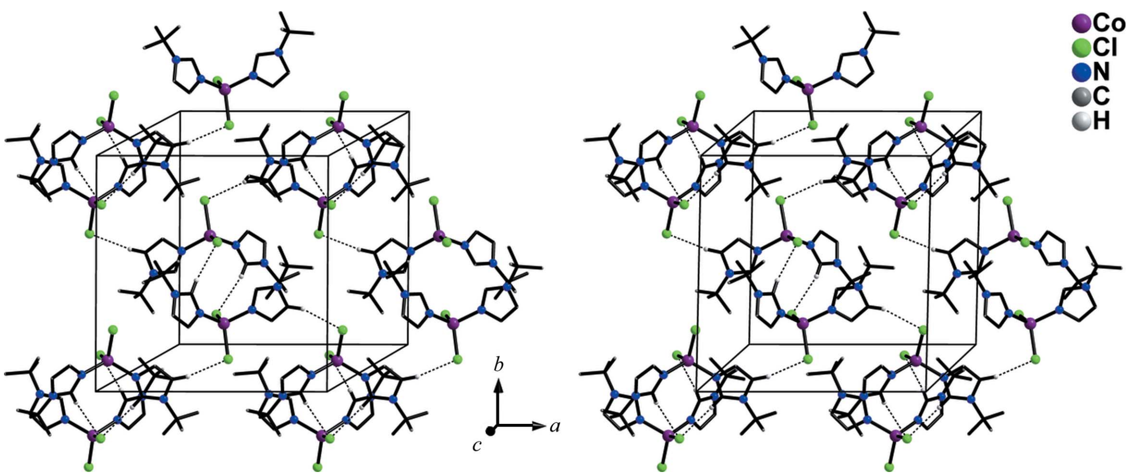


Figure 3
A stereoview of (I), showing the hydrogen-bonding network. Dashed lines indicate hydrogen bonds.

reaction conditions but decomposes relatively quickly. The H atoms in the methylene bridge are acidic and not stable towards the base potassium bis(trimethylsilyl)amide (KHMDS), as we found large amounts of *tert*-butylimidazole in the solution. These form the observed product, which crystallized from the tetrahydrofuran solution. As a consequence of their acidity, imidazole atoms H11, H31, H81, H211, H231 and H281 take part in C—H$\cdots$Cl contacts (Table 2 and Figs. 2 and 3). Six contacts are shorter than the sum of the relevant van der Waals radii (2.95 Å; Bondi, 1964).

The most striking feature of (I) in the solid state is a head-to-tail arrangement of molecules *A* and *B*. Atoms Cl1 and Cl3 of both molecules take part in bifurcated hydrogen-bond bridges (Fig. 2). These dimers connect to form an infinite double layer parallel to the *ab* plane *via* Cl2$^{ii}\cdots$H231 and Cl4$^{i}\cdots$H31 contacts (Fig. 3; symmetry codes are as in Table 2).

Experimental

The bis-imidazolium salt was previously deprotonated by sodium hexamethyldisilazan in tetrahydrofuran and the formation of the free carbene could be independently confirmed (Douthwaite *et al.*, 1999). The corresponding nickel and palladium N-heterocyclic carbene (NHC) complexes have been described in the literature (Douthwaite *et al.*, 2001, 2002) and the addition of sulfur leads to the dithiones (Caballero *et al.*, 2001; Herrmann *et al.*, 1996). However, in this instance, the addition of bis(triphenylphosphane)cobalt(II) chloride (Cotton *et al.*, 1961) did not lead to the expected formation of the bis-carbene complex, and instead we isolated the *N*-coordinated complex, (I). Crystals of (I) suitable for single-crystal X-ray diffraction were grown by diffusion of tetrahydrofuran into a toluene solution of (I). The crystal selected for analysis was fixed in a capillary with perfluorinated ether and transferred to the diffractometer.

Crystal data

$[CoCl_2(C_7H_{12}N_2)_2]$
$M_r = 378.20$
Monoclinic, $P2_1/c$
$a = 14.1054$ (1) Å
$b = 14.5470$ (1) Å
$c = 18.7059$ (2) Å
$\beta = 106.9542$ (3)°
$V = 3671.47$ (5) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 1.23$ mm^{-1}
$T = 173$ K
0.33 × 0.33 × 0.05 mm

Table 1
Selected geometric parameters (Å, °).

Co1—N1	2.0128 (17)	Co2—N23	2.0110 (19)
Co1—N3	2.0191 (17)	Co2—N21	2.0185 (19)
Co1—Cl1	2.2587 (6)	Co2—Cl4	2.2699 (6)
Co1—Cl2	2.2604 (6)	Co2—Cl3	2.2757 (7)
N1—Co1—N3	109.65 (7)	N23—Co2—N21	116.50 (8)
N1—Co1—Cl1	109.36 (5)	N23—Co2—Cl4	104.23 (6)
N3—Co1—Cl1	110.70 (6)	N21—Co2—Cl4	105.72 (6)
N1—Co1—Cl2	104.51 (5)	N23—Co2—Cl3	108.64 (6)
N3—Co1—Cl2	105.03 (5)	N21—Co2—Cl3	106.16 (6)
Cl1—Co1—Cl2	117.25 (2)	Cl4—Co2—Cl3	115.96 (3)
Cl1—Co1—N1—C1	78.18 (18)	Cl3—Co2—N21—C21	−64.6 (2)
Cl1—Co1—N1—C2	−102.57 (16)	Cl3—Co2—N21—C22	100.1 (2)
Cl2—Co1—N1—C1	−155.51 (17)	Cl4—Co2—N21—C21	171.7 (2)
Cl2—Co1—N1—C2	23.74 (17)	Cl4—Co2—N21—C22	−23.6 (2)
Cl1—Co1—N3—C8	−56.1 (2)	Cl3—Co2—N23—C28	53.7 (2)
Cl1—Co1—N3—C9	123.24 (17)	Cl3—Co2—N23—C29	−119.31 (19)
Cl2—Co1—N3—C8	176.49 (19)	Cl4—Co2—N23—C28	178.0 (2)
Cl2—Co1—N3—C9	−4.23 (19)	Cl4—Co2—N23—C29	4.9 (2)

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan [applied during the scaling procedure (*DENZO*; Otwinowski & Minor, 1997)]
$T_{min} = 0.857$, $T_{max} = 1.000$
74460 measured reflections
6741 independent reflections
5547 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.076$
$S = 1.03$
6741 reflections
391 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

H atoms were constrained to an ideal geometry using the standard riding model implemented in *SHELXL97* (Sheldrick, 2008). H atoms were fixed with C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms or C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atoms.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*;

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Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C1—H11⋯Cl3	0.95	2.82	3.767 (2)	172
C3—H31⋯Cl4^{i}	0.95	2.78	3.704 (2)	166
C8—H81⋯Cl3	0.95	2.73	3.618 (2)	157
C21—H211⋯Cl1	0.95	2.73	3.669 (2)	169
C23—H231⋯Cl2^{ii}	0.95	2.75	3.671 (3)	164
C28—H281⋯Cl1	0.95	2.80	3.643 (2)	148

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$.

program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *WinGX* (Farrugia, 1999) and *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2010) and *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

The authors are grateful for support from the Deutsche Forschungsgemeinschaft (DFG) (grant No. STR 526/7–2).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3092). Services for accessing these data are described at the back of the journal.

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